

THE VALENCE OF CHLORINE AS DETERMINED FROM THE MOLECULAR COHESION OF CHLORINE COMPOUNDS

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Since molecular cohesion is a function of the molecular weight and the number of valences in the molecule,¹ we may use the cohesion for the purpose of determining the valence of elements; and in this paper I shall consider chlorine, although something will be said, also, about the other halogens.

It is generally believed, at the present time, that the valence of chlorine is not fixed, but varies in different compounds from one to seven. In its organic, and some inorganic compounds, and in its elemental form it is generally represented as univalent; whereas in the chlorates it is supposed to be pentavalent; and in the perchlorates it is heptavalent.

That chlorine even in such compounds as chloroform, where it replaces univalent hydrogen, may not be univalent is indicated by the action of chlorine compounds on light. Drude,² reasoning that it must be the valence electrons of compounds which would have a period of vibration sufficiently long to respond to light waves, worked out a modification of the Ketteler-Helmholtz dispersion formula which enabled an approximate computation of the number of electrons influencing dispersion in the molecule. He found that in many cases this number was close to the total number of valences in the molecule; but in the case of compounds containing chlorine and fluorine, the number of such light-refracting valences was always greater than in the corresponding hydrogen compounds, and he inferred from this that

¹ Mathews: "The Relation of the Constant "*a*" of van der Waals' Equation to the Molecular Weight and the Number of Valences in the Molecule," Jour. Phys. Chem., **17**, 181 (1913).

² Drude: "Optische Eigenschaften und Elektronen Theorie," Annalen der Physik, [4], **14**, 677 (1904).

these elements must be polyvalent, and not monovalent, as they were usually supposed to be. This conclusion of Drude's was confirmed by Pascal¹ both by the dispersion method of computing valence and by a study of the diamagnetic properties of halogen compounds, the diamagnetic properties having been shown to be related to the number of valences in the molecule. Pascal concluded that fluorine, in organic compounds at any rate, was univalent; but chlorine and the other halogens were polyvalent, and probably chlorine was trivalent. Traube,² in a study of the relationship between the molecular refraction of compounds and the number of their valences, found that for most compounds the molecular refraction of Brühl divided by the number of valences in the molecule was a constant, or nearly such, in all saturated compounds; but in the case of molecules containing the halogens it was necessary to ascribe several valences to the halogens to obtain this constant. He attributed seven valences to chlorine, and had to make still other assumptions for bromine and iodine to bring them into line.

Several chemists, also, have in the past ascribed several valences to chlorine. Thus Meldola³ wrote the formula of methylether hydrochloride, in the form $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \rangle \text{O} = \text{Cl}-\text{H}$, with chlorine trivalent; Nef⁴ represented elemental chlorine as trivalent, but combined chlorine generally as monovalent; and recently Thiele⁵ has especially emphasized the reserve, or extra, valences of iodine and bromine, although, as a rule, he represents chlorine as univalent. Even in sodium chloride it is not certain that the chlorine is univalent, since it is

¹ Pascal: "Recherches magnéto-chimiques sur la structure atomique des halogènes," *Comptes rendus*, **152**, 862 (1911); "Sur un mode de contrôle optique des analyses magnéto-chimiques," *Ibid.*, **152**, 1852 (1911).

² Traube: "Valency, Lichtbrechung u. volume," *Ber. chem. Ges. Berlin*, **40**, 130 (1907).

³ Meldola: I have mislaid this reference and have not been able to find it again.

⁴ Nef: *Liebig's Ann.*, **298**, 205 (1897).

⁵ Thiele and Peter: *Ber. chem. Ges. Berlin*, **38**, 2842 (1905).

known that sodium chloride will add iodine, presumably by the extra valences of the chlorine.¹

There is good ground, therefore, for doubting whether chlorine is ever monovalent. This question can be tested easily by the cohesion method.

Before proceeding to the actual computations it must be decided whether the cohesion method detects only valences actually employed in binding atoms together, or stretching between the atoms; or whether it detects in addition the reserve valences; and also valences which do not extend to atoms, but which are open, in an active form, and ready to combine if the opportunity arises. It is clear from my former paper that concealed, polarized, resting or reserved valences do not play any part in cohesion; or, at any rate, they are not to be counted in the number of valences affecting the cohesion. Thus oxygen has certainly two reserve valences which are usually in an inactive or resting state. In many compounds examined, not more than two valences could be attributed to the oxygen as affecting its cohesion. These two reserve valences played no rôle as long as they were inactive. Similarly, nitrogen has the power of opening up at least seven valences, but it was actually found that only one, two or three valences played a rôle in the cohesion of the nitrogen compounds, depending on how many active valences the atom had. The reserve, or inactive, valences played no part. Carbon is usually quadrivalent, but it is suspected of having the power of becoming hexavalent; but the number of valences active in carbon compounds was always two, or four. If these reserve valences of carbon exist they do not affect cohesion. Sulphur, too, although it may be hexavalent, has only four of its valences playing a part in the cohesion of sulphur dioxide; the two reserve valences are inactive on the cohesion.

It is clear, then, that the cohesion does not detect, and consequently it is not affected by, those reserve valences which are polarized, or resting, or, which are, as it were, like antennae, withdrawn or folded, within the atom.

¹ See Friend: "The Theory of Valency," London, 1909, pp. 58 et seq.

But valences may conceivably exist in an active state not stretching between atoms, but extending outward from the atom and in a condition to unite with other atoms. These are active valences. For example, we may expect the valences on the atoms of a dissociated, monovalent gas to be in this condition. Such atoms would naturally be very active chemically and we should expect the cohesion of such particles to be affected by this condition. There are many evidences that this is actually the case and that valences of this kind are detected by cohesion and will be included in the number of valences computed from the cohesion as existing in the molecule. This is well shown in the argon group, which I shall discuss later, in which it appears that there are two such active valences in argon, krypton, and probably xenon. It appears to be the case, too, in unoxidized sulphur compounds such as ethyl sulphide, as I shall show in a subsequent paper. And there is evidence elsewhere that these open or active valences affect cohesion, although they do not stretch between the atoms of the same molecule. It is, then, active valences, and valences actually employed in binding together the atoms of the molecule, which affect molecular cohesion. It is only the number of such valences which the cohesion enables us to compute, and it is, of course, exactly for this reason that the method has so great a value.

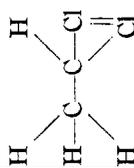
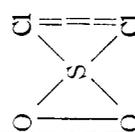
We may then be certain that if we find the valence of chlorine to be three and the compounds are not associating, those three valences are not free, but are actually extending between atoms in the molecule, and if we wish an accurate graphic formula of the compound we must represent these ties.

The method of measuring the number of valences is to compute the number from "*a*" of van der Waals' equation, or from what I have called the square of the cohesive mass, or M^2K , a factor which is equal to "*a*", divided by the square of the number of molecules in the volume of fluid for which "*a*" has been taken. The method of computing M^2K is given in the previous paper. The formula employed is $M^2K = 2.98 \times 10^{-37} (\text{Mol. Wt.} \times \text{Valences})^{2/3}$. Or: Number of Valences = $(M^2K)^{3/2} \times 6.147 \times 10^{34} / (\text{Mol. Wt.})$.

TABLE I.—THEORETICAL AND COMPUTED NUMBER OF VALENCES IN CHLORINE COMPOUNDS

1 Substance	2 Formula	3 $\log_{10} M^{\circ}K$	4 Mol. wt.	5 Computed No. of valences	Theoretical No. of valences		8 Graphic formula
					6 $Cl=3$	7 $Cl=1$	
1 Carbon tetrachloride	CCl_4	-35.74247	153.8	16.4	16	8	
2 Stannic chloride	$SnCl_4$	-35.87500	260.8	15.3	16	8	
3 Germanium tetrachloride	$GeCl_4$	-35.79817	214.3	14.3	16	8	
4 Chlorobenzene	C_6H_5Cl	-35.84615	112.45	32.1	32	30	
5 Chloroform	$CHCl_3$	-35.61128	119.35	13.5	14	8	
6 Methyl chloride	CH_3Cl	-35.26811	50.45	9.7	10	8	

TABLE I (Continued)

7	Propyl chloride	C_3H_7Cl	-35.59465	78.45	19.7	22		
8	Ethyl chloride	C_2H_5Cl	-35.49356	64.45	16.6	16		
9	Ethylidene chloride	$C_2H_4Cl_2$	-35.63725	98.9	17.8	18		
10	Ethylene chloride	$C_2H_4Cl_2$	35.67488	98.9	20.2	18		
11	Chlorine	Cl_2	35.22351	70.9	5.9	6		$Cl \equiv Cl$
12	*Silicon tetrachloride	$SiCl_4$	-35.74648	170.2	15.1	16		
13	*Thiosulphuryl chloride	S_2Cl_2	-35.76597	134.9	20.3	18		
14	*Acetyl chloride	CH_3COCl	-35.55497	78.45	16.8	16		
15	*Chloretethyl formate	$C_3H_5ClO_2$	-35.74968	108.45	23.9	24		
16	*Chloral	CCl_3CHO	35.73899	147.35	16.9	20		
17	*Thionyl chloride	$SOCl_2$	-35.63793	118.9	14.8	14		
18	*Sulphuryl chloride	SO_2Cl_2	-35.65648	134.9	14.1	14		
19	*Phosphorus trichloride	PCl_3	-35.70915	137.35	16.4	16		$P = 7$
20	*Phosphorus oxychloride	$POCl_3$	-35.76967	153.35	18.1	18		$P = 7$
21	Hydrochloric acid	HCl	-35.88550	36.45	3.6	4		Associates
22	Bromine	Br_2	-35.14659	159.92	2.0	6		$Br-Br$
23	Brombenzene	C_6H_5Br	-35.89265	157	27.0	32		
24	Iodobenzene	C_6H_5I	-35.96071	204	26.4	32		
25	*Ethyl iodide	C_2H_5I	-35.67614	155.85	12.9	16		

*Compounds marked * have V_c and T_c computed from the surface tension, and M^3K is not so accurate as when V_c and T_c are directly determined. For the method of computation see the preceding paper.

Some association. $S = 6$

To show how closely these compounds yield the constant "c," where $c = M^2K / (\text{Mol. Wt.} \times \text{Valences})^{2/3}$, Table II is appended. "C" was found in a previous paper to be about 2.98×10^{-37} for other than chlorine compounds. Chlorine is throughout considered as trivalent.

TABLE II.—"C" CALCULATED FOR CHLORINE COMPOUNDS. CL CONSIDERED TRIVALENT EXCEPT IN HYDROCHLORIC ACID AND PROPYL CHLORIDE

	Substance	Formula	Valence	$C \times 10^{37}$	Remarks
1	Carbon tetrachloride	CCl_4	16	3.03	
2	Stannic tetrachloride	SnCl_4	16	2.91	
3	Germanium tetrachloride	GeCl_4	16	2.78	All 4 chlorines trivalent
4	Silicon tetrachloride	SiCl_4	16	2.86	
5	Chloroform	CHCl_3	14	2.90	
6	Methyl chloride	CH_3Cl	10	2.97	
7	Chlorine	Cl_2	6	2.96	
8	Ethyl chloride	$\text{C}_2\text{H}_5\text{Cl}$	16	3.06	
9	Ethylene chloride	$\text{C}_2\text{H}_4\text{Cl}_2$	18	3.15	
10	Ethylidene chloride	$\text{C}_2\text{H}_3\text{Cl}_2$	18	3.02	
11	Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	32	2.98	
12	Thiosulphuryl chloride	S_2Cl_2	18	3.23	Some association
13	Acetyl chloride	CH_3COCl	16	3.08	Slight association
14	Chlorethyl formate	$\text{C}_3\text{H}_5\text{ClO}_2$	24	2.96	
15	Chloral	CCl_3CHO	20	2.67	
16	Thionyl chloride	SOCl_2	14	3.09	Slight association (sulphur hexavalent)
17	Sulphuryl chloride	SO_2Cl_2	14	2.97	Sulphur quadrivalent
18	Propyl chloride	$\text{C}_3\text{H}_7\text{Cl}$	21	2.93	
19	Phosphorus trichloride	PCl_3	16	3.03	
20	Phosphorus oxychloride	POCl_3	18	2.99	
21	Hydrochloric acid	HCl	2	3.24	Association (?)

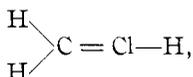
Mean (omitting HCl, S_2Cl_2 and CCl_3CHO), 2.99

The answer to the question whether chlorine is trivalent or monovalent is given in no indecisive manner by the method

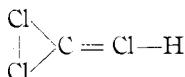
of determining the valence from the cohesion, as is shown in columns 5 and 6 of Table I. With three possible exceptions, chlorine is seen to be everywhere trivalent. The possible exceptions are hydrochloric acid, propyl chloride and one of the chlorine atoms in germanium tetrachloride. In the first, association renders the valence of the chlorine somewhat doubtful; in other words, here also chlorine may be trivalent. In the second, propyl chloride, the critical data may be wrong. They were determined in 1886 by Vincent and Chappuis, and the other determinations by these authors give generally a value for "*a*" slightly lower than is to be expected. It is not impossible, therefore, that a redetermination of the critical data for this substance will make M^2K sufficiently high to make the chlorine trivalent. For the third substance, germanium tetrachloride, I can find but one determination of the critical data in 1887. It is not unlikely, therefore, that the data will need some revision. This method of determining the valence of chlorine confirms, therefore, the conclusions of Pascal, based on the study of the dispersion and the magnetic properties, that chlorine is polyvalent, and, further, this method shows it to be beyond doubt generally trivalent.

Moreover, since nearly all these compounds are normal and not associating, the valences of the chlorine are shown to be not resting, or in reserve, and not dissociated active valences, but actually extending between the atoms of the molecule. I have indicated in column 8 of Table I, some possible structural formulae showing how these valences may be extending in the molecule. Where there are two or more chlorine atoms in the molecule, no serious reconstruction of the graphic formulae is required, since the extra valences may be pictured as reaching between the chlorine atoms; but where there is an odd number of chlorine atoms in the molecule, or where there is but a single one, then a fundamental change must occur in the graphic formula. For example, in ethyl and methyl chlorides, the formula must be written as I have indicated, with the chlorine joining the carbon by two bonds

and with one hydrogen united to the chlorine. I do not wish to lay stress on this point until by a careful determination of the critical data the number of valences in the molecule shall have been exactly determined, but it may be pointed out that, if methyl chloride be written as:



the reason why it decomposes into methylene and hydrochloric acid appears at a glance, since such a double bond is always a source of weakness; and similarly with ethyl chloride, which would be in reality ethylidene chlorhydrate, decomposing into ethylidene and hydrochloric acid. One can also more easily understand in this way the decomposition of chloroform into dichloro-methylene and hydrochloric acid, as the formula



shows. Phosgen will arise from the dichlormethylene uniting with oxygen.

The evidence, then, from such various sources as the behavior toward light, the diamagnetic properties and cohesion is unanimous that chlorine is polyvalent and not monovalent; many of the chemical and physiological properties of chlorine compounds are also more easily understood on the hypothesis of its trivalency. We may, therefore, conclude that in all these compounds chlorine is trivalent.

The question which must now be settled is no longer whether chlorine is trivalent, but whether it is ever monovalent. It is certainly trivalent in most of these compounds in which it was supposed to be monovalent; it is trivalent even in its elemental state. It remains to be seen whether it is ever monovalent. In hydrochloric acid it would appear to be monovalent; but it is exactly here that association takes place. Is it without significance that exactly that compound associates which has but one of the valences of the chlorine

satisfied by another monovalent atom? Is it not rather more probable that this is the cause of its association, the other two valences being not closed, but out and active? The computation actually shows that the chlorine is here also trivalent. I know of no means of telling whether it is monovalent or trivalent in sodium chloride. But it is not impossible that sodium chloride itself is a highly associated substance. Furthermore, its power of adding iodine indicates that the chlorine may be trivalent. Friend also states that sodium chloride may be $\text{Na} - \text{Cl} = \text{Cl} - \text{Na}$.

Concerning the valence of the other halogens, the facts are too scanty and the data too unreliable to draw a conclusion from the cohesion, except perhaps in the case of elemental bromine, which appears to be univalent. The critical data of brombenzene and iodobenzene were not directly determined by Young, but computed from the temperature, pressure and density curves. I do not believe that they are entirely trustworthy, since the number of valences found in the molecule is too small even if these halogens are considered monovalent, unless the carbon be here trivalent, and this does not seem possible. T_c and V_c of ethyl iodide, I computed from Ramsay and Shields' surface-tension determinations, and this computation is not very accurate. Hence I do not attach much weight to the cohesive evidence of the valence of any of these compounds of bromine and iodine. There are no indications, however, that they are polyvalent. That they are polyvalent is, however, indicated from their action on light, their diamagnetic properties and many of their chemical properties. Inasmuch, however, as the refraction method is not very satisfactory for determining valence, the question of the valence of these substances must be left open, with the probability that they will be found to be polyvalent like chlorine.¹

¹ The fact that bromine is monovalent in its elemental state may account for its relative inertness and is confirmed by its dissociation at high temperatures, when the atoms have been shown to have but one active valence. See Friend: "The Theory of Valence," 1909, p. 18.

Fluorine is apparently monovalent in fluorbenzene, since even with fluorine monovalent the number of valences computed from the cohesion is still too small. For this I can give no reason since the critical data of this substance seem to be accurately known. In methyl fluoride the total valences are computed as 9, whereas there should be 10 if fluorine is trivalent and 8 if it is monovalent. Pascal found fluorine to be monovalent by the magnetic and optical method; but Drude, from the optical behavior of calcium fluoride, believed it to be polyvalent. The critical data of more fluorine compounds must be accurately determined before the cohesional method can determine the valence of fluorine. The chemical behavior of hydrogen fluoride leaves no doubt that in it fluorine is polyvalent.

There is still another interesting conclusion from this study: it appears that all substances, and only those substances, associate, which are found by this method to contain active, free valences. I believe we may here have the explanation of the cause of association; and possibly the reason why associating substances dissolve in other associating liquids and are there normal, but as this is a separate problem in itself, I shall hope to return to it later.

Summary and Conclusion

1. If the valence of chlorine be determined by the cohesional method it is found to be trivalent in its elemental state and in nearly all the compounds examined. The three valences of the chlorine in these compounds are not reserve valences, but are all in action and extending between the atoms of the molecule. Graphic formulae have been suggested based on this fact.

2. This result is in harmony with the determination of the valence of chlorine by the diamagnetic and refraction method.

3. The valence of fluorine is more doubtful, but appears to be unity in fluorbenzene. Bromine has unity valence in its elemental form. The valence of iodine and bromine in

their compounds cannot be definitely determined from their cohesion on account of the inadequacy of the critical data.

4. The cohesional method detects two kinds of valences, namely, valences actually extending between the atoms and active in binding the atoms together; and valences active or open, which are in a position to unite, but to which no atoms are attached. Reserved, or resting, valences play no part as valences in molecular cohesion.

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